STYRENE-BUTADIENE COPOLYMERS: MECHANISM OF MERCAPTAN MODIFICATION

BY

JOHN MATHEWS STEWART

B. A, Montana State University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

In the copolymerization of butadiene and styrene in an aqueous emulsion, the presence of a substance known as a "modifier" has been found necessary to produce a rubber substitute which can be easily milled and processed. In the preparation of GR-S, lauryl mercaptan is the standard modifier. Precise knowledge concerning the mechanism of modification would be expected to facilitate progress in the development of still better modifiers and to permit more effective use of the agents now available. The present work was undertaken in an effort to supply this knowledge.

Experimental and Discussion

The use of relatively large amounts of lauryl mercaptan in both bulk and emulsion polymerizations of styrene and butadiene resulted in polymers of low molecular weight. Sulfur analyses and cryoscopic molecular weight determinations on these polymers revealed the following facts:

(1) The use of increasing amounts of lauryl mercaptan in the polymerizations successively decreased the molecular weight of the polymers obtained.

(2) As the molecular weight of the polymers decreased, the percentage of sulfur present correspondingly increased.

(3) Comparison of sulfur analyses and molecular weight measurements of the purified polymers showed the ratio of sulfur atoms per polymeric molecule to be nearly 1:1 in the case of polystyrene. The low molecular weight polybutadienes were much more difficult to handle experimentally. The number of sulfur atoms per polymeric molecule varied from 0.45 to 0.8, but because of the experimental difficulties the results are not as reliable as those obtained on polystyrene.

Commercial GR-S samples were partially fractionated to re-

move very high and very low molecular weight measurements were carried out on the middle fractions. Results incidate that the ratio of sulfur atoms to molecular weight in GR-S is very nearly 1:1.

To determine whether the entire dodecanethiol radical entered the polymer chain, various methods of cleavage of the polymers were used. Cleavage with chlorine and water, according to the method of Lee and Dougherty for the cleavage of organic sulfides,[1] was unsuccessful for low molecular weight polystyrene. However, an oil having a molecular weight and sulful analysis close to that of a compound having one molecule of mercaptan combined with two molecules of butadiene were cleaved with chlorine and water to give n-dodecanesulfonyl chloride.

A modification of the method of Mozingo, Wolf, Harris and Folkers[2] for the hydrogenolysis of organic sulfides by Raney nickel was also used. Low molecular weight styrene and GR-S samples were cleaved to give n-dodecane.

Further evidence for the presence of the entire modifier radical in the polymer was obtained by the study of polymerizations with mercaptan modifiers containing other functional groups. In polystyrenes prepared with thioglycolic acid and ethyl thioglycolate as modifiers, the ratio of sulfur atoms to carboxyl or carbethoxyl groups were nearly 1:1. Comparison of sulfur analyses, neutral or saponification equivalents, and osmotic molecular weight measurements indicated that these polymers contained approximately one modifier residue per polymeric molecule.

Study of the experimental results indicates that in the polymerization of styrene, butadiene, and the copolymerization of these monomers in the presence of lauryl mercaptan as modifier the mercaptan acts through a free radical mechanism as a chain transfer agent, terminating the growth of one polymer chain and starting another.

A similar investigation was begun on the modification of polymers by diisopropyl xanthogen disulfide. Use of increasing amounts of this modifier in bulk and emulsion polymerizations

of styrene gave polymers of progressively decreasing molecular weight and progressively increasing sulfide content. The number of sulfur atoms per polymeric molecule varied from one to two in polystyrene prepared by the bulk method, with benzoyl peroxide as catalyst, and was nearly always two for polystyrene prepared in emulsion, with potassium persulfate as catalyst.

Bibliography

[1] Lee and Dougherty, J. Org. Chem 183, (1940).

[2] Mozingo, Wolf, Harris and Folkers, J. Am. Chem. Soc. 65, 1013 (1943).

VITA

The author was born in Vermillion, South Dakota, on April 5, 1920. He attended the public schools of Sioux City, Iowa, and Missoula, Montana, and graduated from the Missoula County High School in June, 1937. He enrolled in the University of Washington in September of that year. In January, 1938, he transferred to Montana State University from which he received the degree of Bachelor of Arts in Chemistry in June, 1941. In the fall of the same year he enrolled in the graduate school of the University of Illinois, where he held a teaching assistantship in chemistry from September, 1941 to June, 1942. From September, 1942, to date, he has held a Special Research Assistantship.

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